

## Ionic strength dependence of stability constant. Part 2: Spectrophotometric study of the dioxyvanadium + leucine system in the range $0.1 \leq I \leq 1.0$

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**Abstract.** The dioxyvanadium + leucine system has been investigated by a combination of spectrophotometric and potentiometric methods at  $25 \pm 0.1^\circ\text{C}$  and ionic strengths ranging from 0.1 to 1.0 mol dm<sup>-3</sup> with NaClO<sub>4</sub> as a background salt in the pH range 1.3–2.5, with high ligand-to-metal ratios. Parameters for dependence on ionic strength have been obtained for the protonation constant of leucine.

**Keywords.** Dioxyvanadium; leucine; ionic strength; stability constant.

### 1. Introduction

Pursuing our systematic study on stability constants (Khorrami *et al* 1992; Gharib *et al* 1993, 1995; Khorrami and Gharib 1995), we reported earlier some features of absorbance as a function of pH (Beck and Nagypal 1990). However, there are few quantitative studies on protonation constants of amino acids at different ionic strengths (Stefano *et al* 1994).

We thought it interesting to investigate the dependence on ionic strengths of protonation constant of leucine and the complexation of dioxyvanadium (V) with this ligand by a combination of spectrophotometric and potentiometric methods in different ionic strengths ranging from 0.1 to 1.0 mol dm<sup>-3</sup> with NaClO<sub>4</sub> as background salt in acidic solution.

### 2. Experimental

**Reagents:** Sodium perchlorate, perchloric acid, L-leucine and sodium hydroxide were obtained from E Merck. Sodium metavanadate was from Riedle-De Haenag Seelz, Hanover as analytical reagent grade material. All materials were used without further purification. Dilute perchloric acid solution was standardized against KHCO<sub>3</sub>. A 50 mass% sodium hydroxide solution, free from carbonate, was prepared from analytical grade material filtered through a G4 Jena glass filter. Vanadium (V) solutions were standardized titrimetrically against a standard iron (II) sulphate solution (Zare *et al* 1979).

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**Measurements:** A Horiba pH meter F-12 was used for pH measurements. Spectrophotometric measurements were performed on a UV-Vis Shimadzu 2101-PC spectrophotometer with an AcerMat 486 SX/250 computer, using thermostatically matched 10 mm quartz cells. The measurement cell was flow type. A masterflex pump allowed circulation of the solution under study from the potentiometric cell to the spectrophotometric cell so that the absorbance and pH of the solution could be measured simultaneously. All measurements were carried out at  $(25 \pm 0.1)^\circ\text{C}$  and at ionic strengths ranging from 0.1 to  $1.0 \text{ mol dm}^{-3}$  (sodium perchlorate).

### 3. Results and discussion

The equilibrium constant was studied (Itoh *et al* 1975),

$$K_p = \frac{[\text{HL}]}{[\text{H}_3\text{O}^+][\text{L}^-]}, \quad (1)$$

where L represents the fully dissociated ligand anion.

The protonation constants,  $K_p$ , have been determined using potentiometric methods at various ionic strengths and are calculated using a nonlinear least-squares method. The logarithms of protonation constants of the ligand under study are collected in table 1. The dependence of these values on ionic strength can be described by the general equation (Daniele *et al* 1983, 1985),

$$\begin{aligned} \log K_p(I) = \log K_p(I') - AZ^* \left( \frac{I^{1/2}}{1 + BI^{1/2}} - \frac{I'^{1/2}}{1 + BI'^{1/2}} \right) \\ + C(I - I') + D(I^{3/2} - I'^{3/2}) \end{aligned} \quad (2)$$

where,

$$A = 0.5115 + 8.885 \times 10^{-4}(t - 25) + 2.953 \times 10^{-6}(t - 25)^2, \quad (3)$$

$$B = 1.489 + 8.772 \times 10^{-4}(t - 25) + 4.693 \times 10^{-6}(t - 25)^2, \quad (4)$$

and where  $t$  is temperature (deg. Celsius).  $I$  and  $I'$  represent the actual and reference ionic strengths, respectively.  $Z^*$  is the charge on L. Considering that  $A = 0.5115 \text{ M}^{-1/2}$  and  $B = 1.489 \text{ cm}^{-1}$  at  $25^\circ\text{C}$ , (2) can be simplified as,

$$\begin{aligned} \log K_p(I) = \log K_p(I') - Z^* \left( \frac{I^{1/2}}{2 + 3I^{1/2}} - \frac{I'^{1/2}}{2 + 3I'^{1/2}} \right) \\ + C(I - I') + D(I^{3/2} - I'^{3/2}). \end{aligned} \quad (5)$$

$C$  and  $D$  are empirical coefficients whose values are 0.553 and  $-0.568$  from (5), respectively. Dependence on ionic strength for the protonation constant of leucine in  $\text{NaClO}_4$  aqueous solution is shown in figure 1. In the pH range of interest (1.3–2.5),

**Table 1.** Protonation constants of leucine,  $\log K_p$ , at different ionic strengths ( $\text{NaClO}_4$ ).

$I(\text{mol dm}^{-3})$	0.1	0.3	0.4	0.5	0.6	0.8
$\log K_p$	9.78	9.72	9.70	9.64	9.72	9.76

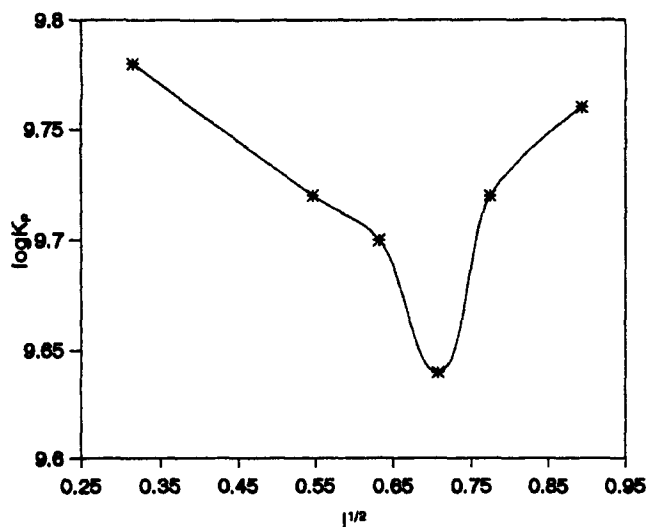


Figure 1. Dependence on ionic strength for the protonation constants in  $\text{NaClO}_4$ .

absorbance and pH were measured for solutions containing V(V) ( $4 \times 10^{-4} \text{ mol dm}^{-3}$ ) with large excess of ligands ( $1 \times 10^{-2} \text{ mol dm}^{-3}$ ).

The formation constant is defined as:

$$K_{\text{VO}_2\text{L}}^{\text{H}} = \frac{[\text{VO}_2\text{H}_{1-m-n}\text{L}^{(m+n-1)-}][\text{H}^+]^n}{[\text{VO}_2^+][\text{H}_{1-m}\text{L}^{m-}]} \quad (6)$$

In this case, data were analyzed by using HL ( $m = 0$ ) as the reactant. It was assumed that only a single complex was formed in the above pH range. The absorbance,  $A$ , at a wavelength of UV range is given by,

$$A = \varepsilon_0[\text{VO}_2^+] + \varepsilon_1[\text{VO}_2\text{H}_{1-n}\text{L}^{(n-1)-}], \quad (7)$$

where  $\varepsilon_0$  and  $\varepsilon_1$  are the molar absorptivities of the vanadyl ion and the complex, respectively. Thus, the formation constant for equation,  $K_{\text{VO}_2\text{L}}^{\text{H}}$ , is given by (Khorrami *et al* 1992; Khorrami and Gharib 1995),

$$\frac{C_{\text{VO}_2}}{A} = \frac{1}{\varepsilon_1} + \frac{(\varepsilon_1 - \varepsilon_0)(A - \varepsilon_0 C_{\text{VO}_2})[\text{H}^+]^n}{A \varepsilon_1 K_{\text{VO}_2\text{L}}^{\text{H}} (\varepsilon_1 C_{\text{HL}} - \varepsilon_0 C_{\text{HL}} - A + \varepsilon_0 C_{\text{VO}_2})} \quad (8)$$

where  $C_{\text{HL}}$  and  $C_{\text{VO}_2}$  are the total concentrations of leucine and  $\text{VO}_2^+$ , respectively. Considering that  $A$  is a function of pH (Itoh *et al* 1975), the values of  $\varepsilon_0$  at  $(25 \pm 0.1)^\circ\text{C}$  and various ionic strengths are shown in table 2.

The number of protons,  $n$ , was determined by applying (8). The straight line plots of  $C_{\text{VO}_2}/A$  against  $(A - \varepsilon_0 C_{\text{VO}_2})[\text{H}^+]^{n/A}$  with  $n = 1$  confirmed the formation of a single complex with the formula  $\text{VO}_2\text{L}$ . The values of the molar absorptivities of the complex,  $\varepsilon_1$ , were determined from the intercept of the plot at various ionic strengths and are shown in table 3.

If we define  $\bar{\varepsilon}$  as (Beck and Nagypal 1990),

$$\bar{\varepsilon} = \varepsilon_0 X_{\text{VO}_2} + \varepsilon_1 X_{\text{VO}_2\text{L}}, \quad (9)$$

**Table 2.** Values of molar absorptivities of the vanadyl ion at various ionic strengths ( $\text{NaClO}_4$ ).

$I$ ( $\text{mol dm}^{-3}$ )	$\lambda_i(\text{nm})$								
	240	245	250	255	260	265	270	275	280
0.1	287	310	320	316	302	283	250	211	178
0.2	245	254	260	263	251	232	208	180	147
0.3	221	231	230	222	210	209	188	160	130
0.4	202	185	214	210	201	188	173	144	118
0.5	168	175	170	166	160	160	142	114	87
0.6	163	173	174	174	169	153	133	107	85
0.8	627	636	612	616	584	568	532	493	452

**Table 3.** Values of molar absorptivities of  $\text{VO}_2\text{L}$  at various ionic strengths ( $\text{NaClO}_4$ ).

$I$ ( $\text{mol dm}^{-3}$ )	$\lambda_i(\text{nm})$								
	240	245	250	255	260	265	270	275	280
0.1	1686	1324	1139	1036	985	949	910	876	819
0.2	1688	1336	1149	1049	999	962	915	878	819
0.3	1740	1403	1222	1115	1070	1020	973	915	846
0.4	1798	1480	1295	1194	1127	1074	1021	962	888
0.5	1901	1542	1349	1294	1175	1138	1078	1020	939
0.6	1962	1598	1402	1345	1227	1172	1133	1066	994
0.8	2108	1758	1583	1477	1392	1322	1238	1154	1059

**Table 4.** Values of  $\log K_{\text{VO}_2\text{L}}^{\text{H}}$  at various ionic strengths ( $\text{NaClO}_4$ ).

$I(\text{mol dm}^{-3})$	0.1	0.3	0.4	0.5	0.6	0.8
$\log K_{\text{VO}_2\text{L}}^{\text{H}}$	0.440	0.395	0.381	0.367	0.340	0.350

or

$$\bar{\epsilon} = \epsilon_0 \left( \frac{\epsilon_1 C_{\text{VO}_2} - A}{C_{\text{VO}_2}(\epsilon_1 - \epsilon_0)} \right) + \epsilon_1 \left( \frac{A - \epsilon_0 C_{\text{VO}_2}}{C_{\text{VO}_2}(\epsilon_1 - \epsilon_0)} \right), \quad (10)$$

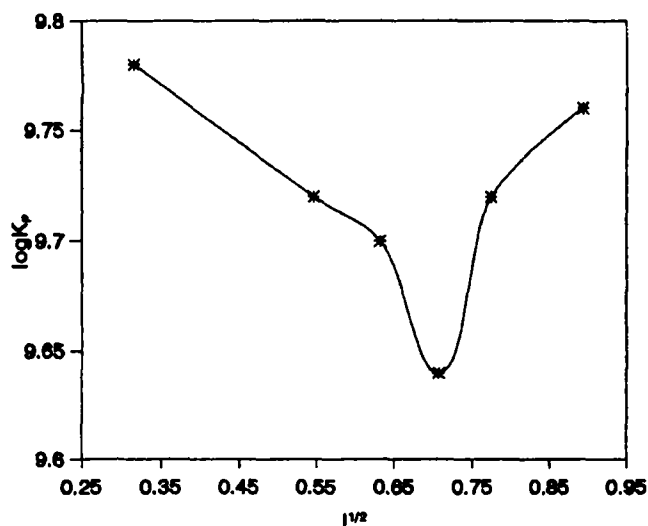
where  $X_{\text{VO}_2}$  and  $X_{\text{VO}_2\text{L}}$  are the mole fractions of the vanadyl ion and the complex, respectively. By the rearrangement of (10), the average ligand numbers,  $\bar{n}$ , can be calculated directly (Beck and Nagypal 1990),

$$\bar{n} = \frac{\bar{\epsilon} - \epsilon_0}{\epsilon_1 - \epsilon_0}. \quad (11)$$

Calculation has shown that  $\bar{n} = 1$ , thus the complex is mononuclear (1:1).  $K_{\text{VO}_2\text{L}}^{\text{H}}$  can be calculated from the slope of (8) and the values of  $\log K_{\text{VO}_2\text{L}}^{\text{H}}$  are collected in table 4. By combining values of  $K_p$  and  $K_{\text{VO}_2\text{L}}^{\text{H}}$ , the stability constant of the  $\text{VO}_2\text{L}$

**Table 5.** Values of  $\log K_{VO,L}^H$  at different ionic strengths ( $\text{NaClO}_4$ ).

$I(\text{mol dm}^{-3})$	0.1	0.3	0.4	0.5	0.6	0.8
$\log K_{VO,L}$	10.220	10.101	10.067	10.001	10.060	10.110

**Figure 2.** Plot of  $\log K_{VO,L}$  against the square root of the ionic strength.

complex can be calculated from (12).

$$K_{VO,L} = K_{VO,L}^H \cdot K_p \quad (12)$$

The values of  $\log K_{VO,L}$  at various ionic strengths are collected in table 5 from figure 2. Figures 1 and 2 show the dependence of  $\log K_p$  and  $\log K_{VO,L}$  on ionic strength. The protonation constant of leucine and the stability constant of the system under study vary with ionic strength. In figure 1,  $\log K_p$  has a larger value at  $I = 0.1$  and a minimum at  $I = 0.5$ . Also  $\log K_{VO,L}$  has a larger value at  $I = 0.1$  and a minimum when the ionic strength approaches 0.5, which is in good agreement with the results obtained for other complexes (Beck and Nagypal 1990).

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